

OXIDATIVE DESULFURIZATION OF LIQUID FUELS

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INTRODUCTION

Among the alternatives of petroleum oil, coal is considered to be one of the most practical energy resources in the next generation, because of its unlocalized abundance. Under such circumstances, the consumption of the fossile fuel such as petroleum oil or coal-derived liquid fuels could be drastically increased in the next decade, and it will take place fatal environmental problems like an acid rain and a global warming. Particularly, the increase of the emission of sulfur oxides due to a combustion of those fuels is seriously concerned in the developing countries. Although it has long been anticipated the development of efficient desulfurization technologies for fossile fuels, except the flue-gas desulfurization processes, most of the research projects seem to be in trouble. In particular, the desulfurization of diesel fuels such as light or heavy oils is going to be critically important to sustaine our modernized life.

we had initiated research projects for developing efficient chemical desulfurization processes of coal, and revealed that the oxidation reaction significantly enhanced the chemical reactivity of the organic sulfur fuctionalities in coal, and it made them easy to remove from a solid coal. For instance, the alkaline fusion under oxygen gas, "Oxy-Alkalinolysis", achieved the sulfur removal upto 95-98% for most of the coals(1). To use such drastic change of the chemical and phisical properties of organic sulfur compounds by oxidation is our strategy for developing an efficient desulfurization process for liquid fuels.

This paper present the results of the study on the desulfurization process using oxidation reactions for liquid fuels.

PROPOSED PRINCIPLE OF OXY-DESULFIRIZATION POR LIQUID FUELS

In general, there are many types of organic sulfur compounds in the fossile fuels. In particular, arylic sulfide-type sulfur and thiophene-type sulfur such as , benzothiophene or dibenzothiophene are believed to be major components(2). These types of organic sulfur atom are known to be chemically so stable that the carbon-sulfur bond-fission does not occur easily. Traditionally, the catalytic hydrogenetaion reaction has been used for such bond cleavage, which has several advantages for industrial purposes, but also some disadvantages. Particularly, the use of hydrogen gas and catalyst forced to take more and more drastic reaction conditions(higher pressure and higher temperature) in order to get the higher degree of the sulfur removal. In Japan, it is assumed that the cost of the capital investment to decrease the sulfur content in a commercial light upto 0.05%-level will be over five hundred billion yen(3). The recent researchs revealed that one of the reason of the difficulty of sulfur removal from a light oil will be the steric hindrance due to the alkyl functions surrounding the sulfur atom in the sulfur compounds. This means that the developement of highly active catalysts may be vital to achieve the long term target , but there seems to be a fatal limitation.

In the meantime, the principle of the proposed oxydative desulfurization process is as follows: It may be very fortunate for us that the most of the organic sulfur atoms in the fossile fuel are thought to be divalent, like a sulfide or thiophene. In general, oxidized sulfur compounds such as sulfoxide or sulfone have

significantly different chemical and physical properties, particularly boiling point and solubility towards various solvents based on a molecular polarity, compared to the corresponding divalent compounds.

Now, an simple idea comes in our mind, that is, a large degree of differences of the boiling point and polarity before and after oxidation should make easy to separate them from other hydrocarbon components through ordinary purification procedures like a distillation, an solvent extraction or/and a chromatographic adsorption.

It can be also emphasized that this process could provide the organic sulfur components in the fuels as a potential low materials to the industrial uses. Namely, our understanding is that the sulfur components in fossil fuels is not a waste. It is a valuable natural resource.

EXPERIMENTAL

Solvents and Reagents: Gold rabel grade reagents were used without further purification.

Sulfur Analyses: High sensitivity sulfur analyzer(Model TS-03, Mitsubishi Kasei Co.) is used for the determination of sulfur content in the liquid fuels.

Oxidation of Liquid Fuels: A typical run as follows. In the three necked flask(300ml) equipped by a mechanical stirrer and reflux condenser, 100ml of liquid fuel was placed, and a mixture of formic acid(10ml) and aqueous hydrogen peroxide (30%, 10ml) was added with vigorous stirring keepin temperature below 60°C for 2 hours. After the reaction the reaction mixture was cooled down at ice-water temperature, and separated the oil layer, and washed by distilled water.

Solvent Extraction: Extraction of sulfur components was carried out by using same amount of liquid fuel and extraction solvent (1/1 vol/vol).

Adsorption: Adsorption of sulfur component in liquid fuel was carried out by using a column chromatography packed by absorbent(silica gel or alumina). The ratio of the liquid fuel and absorbent was 100/10(wt). The sulfur content was determined to the combined liquid passed through the column.

RESULTS AND DISCUSSION

Obviously, the key step of this desulfurization process is the oxidation reaction, which has to selectively oxidize the sulfur atom in the contamination. We have examined many type of oxidants, and found that the peroxyacid, like a performic acid or a pertrifluoro acetic acid, was one of the positive candidate for that. These oxidants are known to oxidize not only sulfur compounds but also olefinic hydrocarbons affording the corresponding epoxy compounds. However, we do not think that this type of the side reaction causes critical damages to the total fuel efficiency.

The reaction mechanism of the oxidation of organic sulfur compound, i.e., dibenzothiophene, by performic acid(a mixture of formic acid and hydrogen peroxide) is illustrated as shown in Figure 1. Namely, formic acid reacts with hydrogen peroxide and gives performic acid and water. Then, the performic acid reacts with dibenzothiophene and gives dibenzothiophene sulfoxide, and a further oxidation gives the corresponding sulfone. Thus overall oxidation reaction consumes only hydrogen peroxide recycling formic acid.

We have initiated this research project from a modeling experiments as follows: A model liquid fuel was prepared by using dibenzothiophene as organic sulfur and cyclohexane as hydrocarbon component. The sulfur content in the model fuel was controlled in 0.30% and it was treated by the mixture of formic acid and aqueous hydrogen peroxide(30%) below 60°C temperature for 2 hours. After the reaction, the mixture was cooled down at 0°C, and resulted white

crystal was filtrated which was determined as dibenzothiophene sulfone. The sulfur content of the filtrate was 0.002%. Then the filtrate was extracted by aqueous dimethylformamide(water content, 3%). The cyclohexane layer was separates an washed with distilled water. After dried over anhydrous magnesium sulfate, the sulfur content was determined as 0.0007%. Also, the filtrate was passed through a silica gel column(oil/silica gel = 100/10 wt/wt). The sulfur content of the eluted solution was 0.0000%(exceeded the detectable limit of the sulfur analyzer Model TS-03, Mitubisikasei Co.)

Based on the results described above, the working principl seems to be correct. It will be also true that the sulfur comonents in liquid fuel such as light oil is not simple like in this model. So that we have applied these procedures to the actual commercial light oil. Figure 2 shows the gas-chromatogram(OV-1, packed glass-column; FPD-detector) of the reaction mixture of dibenzothiophene by this oxidation system. The shift of the retention time of the reaction product(sulfone) clearly suggests the increased boiling point and polarity by oxidation.

Figure 3 shows the gas-chromatogram(OV-1, packed glass-column; FPD-detector) of the reaction mixture of a commercial light oil(sulfur content, 0.56%) before and after oxidation. The wide range of distribution of peaks is observed due to a mixture of alkylderivatives of mainly benzothiophene and dibenzothiophene. Interestingly, there is a significant deference between the retention time in both peak distributions before and after oxidation, which is considered to be resulted by the oxidation as well as shown in Figure 2

Table 1 and 2 show the part of the results examined the sulfur removals of the commercial light oil and its oxidized one, which were achieved by the solvent extraction and the adsorption by silicagel and alumina column-chromatography.

Table 1 Sulfur Removal of Light Oil by Solvent Extraction^{a)}

| Solvent | sulfur content(%) | |
|--------------------|------------------------------------|--------------------|
| | commercial light oil ^{b)} | oxidized light oil |
| Acetonitrile | 0.52 | 0.057 (0.012)* |
| OMFC ^{c)} | 0.49 | 0.018 (0.003)* |

* Trifluoroacetic acid / hydrogen peroxide

a) Ratio of oil and solvent was 1 / 1(vol) and a single extraction

b) Original sulfur content was 0.56%

c) N,N-Dimethylformamide

Table 2 Sulfur Removal of Light Oil by Adsorption^{a)}

| Adsorbent | sulfur content(%) | |
|-----------|------------------------------------|---|
| | commercial light oil ^{b)} | oxidized & extracted(DMF) light oil ^{c)} |
| Silicagel | 0.54 | 0.0046 (0.0009)* |
| Alumina | 0.53 | 0.0038 (0.0005)* |

* Trifluoroacetic acid / hydrogen peroxide

a) Ratio of oil and adsorbent was 100 / 5(wt) , glass column(ϕ =0.5mm)

b) Original sulfur content was 0.56%

c) After extracted by N,N-Dimethylformamide

CONCLUSION

The proposed "Oxy-desulfurization Process" has exhibited a powerful ability to remove sulfur from diesel fuels like a light oil. The characteristic features of this efficient new process can be summarized as follows.

1. High degree of sulfur removal: Possible to down to a ppm-order sulfur-content
2. Mild reaction conditions: Ambient pressure and temperature
3. Useful by-product: Organic sulfur compounds
4. Applicable to heavier oil desulfurization
5. Economical ?

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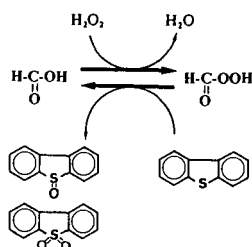


Figure 1 Oxidation reaction mechanism

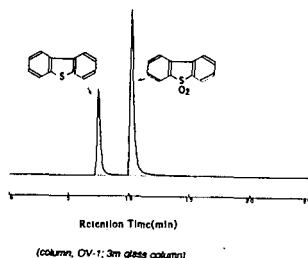


Figure 2. FPD-Gas chromatogram of Model-fuel oxidized by Formic acid/Hydrogen peroxide

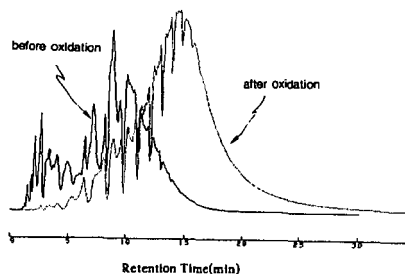


Figure 3 FPD-Chromatogram of Light Oil oxidized by Formic acid/Hydrogen peroxide